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Quarterly Report No. 3

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"A Study of the Decomposition Mechanism of Ammonium Perchlorate"

Prepared by: Departments of Chemistry and Chemical Engineering,
Auburn University.

For the period: 1 January - 31 March 1966

Contract No. DA-01-021-AMC 12346(Z), Part I,

Birmingham Procurement District, U. S. Army.

Administered by: The Auburn Research Foundation

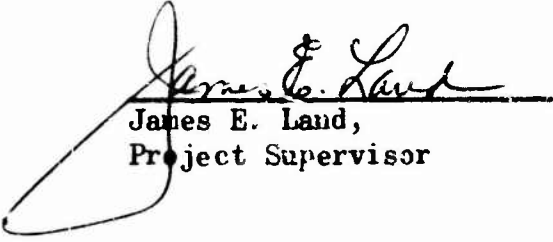
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Quarterly Report On:

"A Study of the Decomposition Mechanism of Ammonium Perchlorate".

Prepared by: Departments of Chemistry and Chemical Engineering,
Auburn University, and submitted by:



James E. Land,
Project Supervisor

For the Period: 1 January - 31 March, 1966

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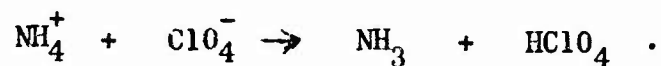
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1. Introduction

The experimental work herein reported is a part of the continuing effort first begun under Contract No. DA-01-009-ORD-1023(Z), Part I designed to provide a better understanding of the mechanism which occurs during the decomposition of ammonium perchlorate (hereinafter abbreviated AP) and the way in which additives influence the rate controlling step.

Differential thermal analysis (DTA) has been used in this study and it is the technique of measuring the heat effects associated with the AP decomposition when the AP is heated from ambient temperature to about 450° C.

The thermal decomposition of AP, which is thought to proceed through a sequence of reactions, undoubtedly in the first step undergoes dissociation as follows:



This reaction is a case where the acid, NH_4^+ , reacts with the base, ClO_4^- , to form the conjugate acid and base species HClO_4 and NH_3 respectively. The stability of these species is a function of temperature, and as the temperature is lowered the stronger acid, HClO_4 , and base, NH_3 , tend to react to form the weaker conjugate pairs*.

(*) "Acids, Bases, and The Chemistry of the Covalent Bond",
by Van der Werf, Reinhold Pub. Co., 1961, page 15.

Another way of interpreting this reaction is to note that there is a competition between the two bases, NH_3 and ClO_4^- , for the proton, H^+ , which Pearson** has designated as a hard acid. He also pointed out, that as a general rule, hard acids and hard bases tend to combine to produce a more stable adduct than the combination of a hard with a soft species.

At room temperature H^+ , the proton, a very hard acid much more readily combines with the base, NH_3 , which is of a harder nature than the ClO_4^- . But with increasing temperature thermal vibrations between the atoms in these groups increase in magnitude. It is thought that the effect of such vibrations is much more pronounced in the NH_3 molecule as compared to the ClO_4^- ion, however, it is difficult to find absolute evidence for this contention. It can be reasoned that heat makes the NH_3 molecule more readily polarizable and consequently its moderately hard base character gives way to a more soft base nature and at a much faster rate than the ClO_4^- ion, so that at about 150°C . and above the latter species is harder and thereby extracts the proton from the ammonium ion substrate to form the stronger adjunct or complex compound.

It is at this point that the next reaction in the

(**) R. G. Pearson, Science, 151, 172(1966) (Also C.E.N., May 31, 1965, p. 90ff.)

sequence of AP decomposition begins with the splitting out of an $[OH]$ or $[O]$ free radical from the unbalanced perchloric acid molecule.

Here, also, is where the catalyst probably plays its vital role, that is, if a softer acid site is presented by it, there will be a tendency for the catalyst to capture the heat created soft base form of NH_3 by electrophillic attack. The adjunct so created between the catalyst and the NH_3 not only helps to further displace the equilibrium of equation (1) more to the right but also will, because of electron drainage from the nitrogen atom, weaken the N-H bonds, thereby making the H's from the NH_3 more susceptible to attack by the $[O]$ and $[OH]$ free radicals coming from the decomposing perchloric acid. With the removal of the H's from the NH_3 the electron pair which bonds the N to the catalyst is no longer prone to continue the nucleophillic attack and the nitrogen leaves the catalyst as free nitrogen or as an oxide thereby making the spot on the catalyst available for a repeat of the sequence of steps.

Based upon these arguments the catalyst to function efficiently should be or contain in its make up a soft acid. Metal ions are Lewis type of acids, so we reasoned that adding such to the AP as metal perchlorate doped samples, we might be able to correlate the results with the respective relative hard and soft acid character of the metal ions.

2. Current Work

During the period of this report our efforts were concerned with a continuation of the making of DTA runs at various heating rates on AP samples which had been doped with a known per cent of a metal perchlorate so as to determine the influence of this additive on the DTA exo- and endotherms recorded for AP decomposition as it is heated at various rates over a given temperature range.

3. Experimental procedure and equipment

The procedures and equipment being employed have been previously described and illustrated in the Final Report of Contract DA-01-009-ORD-1023(Z), Part I.

4. Experimental Materials

The following doped AP samples were subjected to DTA runs:

AP and $\text{Cu}(\text{ClO}_4)_2$;	AP and $\text{Pb}(\text{ClO}_4)_2$;	
AP and KClO_4 ;	AP and $\text{Cd}(\text{ClO}_4)_2$;	AP and $\text{Zn}(\text{ClO}_4)_2$;
AP and $\text{Mn}(\text{ClO}_4)_2$;	AP and AgClO_4 ;	AP and $\text{Ba}(\text{ClO}_4)_2$;
AP and $\text{Hg}(\text{ClO}_4)_2$;	AP and NaClO_4 ;	AP and $\text{Fe}(\text{ClO}_4)_2$.

These were prepared by mixing mole parts of AP with mole parts of the other compound in a water solution either in a 95/5 or 99/1 ratio. The solution was then evaporated to dryness at atmospheric pressure and at a temperature not greater than 100° C. The residue was ground with a hand mortar and pestle and then screened. After screening the samples were again dried at 105° C. for several days then stored under dry conditions until used.

5. Accomplishment of technical objectives.

The third quarter technical objectives as set forth on pages 3 and 4 of the enclosure to the letter of the Director of the Auburn Research Foundation to Mr. William B. Thomas, U. S. Army Missile Command, AMSMI-RMP, dated 21 October 1965 have been completely attained during the period of this report.

6. Tabulated Results

In Tables I and II are recorded the results of DTA runs made with the doped AP samples.

The data in these tables are listed as follows: Column (1) gives the composition of the doped AP sample. All runs were made at atmospheric pressure and open to the air. Column (2) lists the particle size(cf. page 25 of the Final Report for Project 1023(Z), Part I). Column (3) gives our sample number to facilitate locating the DTA plot when needed for reference. Column (4) shows the heating rate in degrees C. per minute. This was the setting on the temperature programmer and was not the measured slope of the heating trace. Columns marked T_1 , T_2 , T_3 , etc. are the peak temperatures in °C. as read from left to right on the DTA plot. Unless otherwise noted T_1 is the crystal transformation in each case and it is endothermic, all others being exothermic.

Table I

Peak temperatures from DTA runs on doped AP samples
(95/5 mole ratio of AP to added metal perchlorate)

(1)	(2)	(3)	(4)	T ₁	T ₂	T ₃	T ₄
Cu(ClO ₄) ₂	F	5-74-2	2	-----	-----	-----	-----
"	F	5-74-1	4	235.1	241.1	-----	-----
"	F	5-75-1	10	239.1	266.5	-----	-----
"	M	5-77-1	2	?	247.0	270.3	-----
"	M	5-76-2	4	240.7	278.2	-----	-----
"	M	5-76-1	10	242.2	273.1	-----	-----
"	C	5-78-3	2	236.3	246.2	268.1	273.1
"	C	5-77-2	4	239.9	264.5	333.2	-----
"	C	5-78-1	10	244.4	280.1	-----	-----
Cd(ClO ₄) ₂	F	5-81-1	2	239.1	281.0	-----	-----
"	F	5-78-2	4	240.7	286.0	-----	-----
"	F	5-79-1	10	245.5	292.6	-----	-----
"	M	5-82-1	2	238.7	286.4	290.0	-----
"(*)	M	5-79-3	4	239.9	287.9	-----	-----
"(*)	M	5-83-1	10	241.1	295.7	377.8	-----
"(*)	C	5-82-2	2	236.3	284.4	287.9	306.8
"(*)	C	5-83-2	4	239.9	283.3	-----	-----
"(*)	C	5-85-2	10	239.1	296.4	368.4	-----
AgClO ₄	F	5-100-1	2	240.0	331.2	-----	-----
"	F	5-99-2	4	238.7	344.6	-----	-----
"	F	6-4-2-	10	239.5	374.7	-----	-----
"	M	6-1-1	2	241.1	329.4	-----	-----
"	M	6-1-2	4	240.3	350.6	-----	-----
"	M	6-6-3	10	241.1	380.1	-----	-----
"	C	6-3-1	2	239.5	277.8	327.5	-----
"	C	6-2-1	4	238.3	325.6	-----	-----
"	C	6-5-2	10	241.4	386.3	-----	-----

(*). A small endotherm was noted in these runs at about 120 degrees.
Such may indicate the loss of water.

Table I (cont.)

(1)	(2)	(3)	(4)	T ₁	T ₂	T ₃	T ₄
Fe(ClO ₄) ₂	F	6-15-2	2	238.7	327.9	-----	-----
"	F	6-16-1	4	240.7	341.9	-----	-----
"	F	6-17-2	10	241.1	358.6	-----	-----
"	L	6-17-1	2	238.3	329.8	-----	-----
"	M	6-16-2	4	237.1	344.2	-----	-----
"	M	6-19-2	10	240.3	358.6	-----	-----
"	C	6-18-1	2	236.6	328.1	-----	-----
"	C	6-16-3	4	235.9	328.6	-----	-----
"	C	6-19-3	10	240.3	348.7	-----	-----
Zn(ClO ₄) ₂	F	5-94-1	2	238.7	247.4	279.4	290.3
"	F	5-91-3	4	244.6	262.2	290.6	-----
"()	F	5-93-1	10	240.0	290.3	-----	-----
"	M	5-94-2	2	237.9	246.2	277.8	289.1
"	M	5-93-2	4	238.3	298.7	304.1	-----
"(**)	M	5-95-3	10	244.2	294.9	316.4	-----
"	C	5-95-1	2	236.3	243.8	272.7	287.9
"(**)	C	5-93-3	4	240.7	281.7	291.4	-----
"(**)	C	5-96-1	10	243.8	288.7	304.1	-----
Mn(ClO ₄) ₂	F	5-95-2	2	229.9(+)	235.1	248.5	323.0
"	F	5-96-2	4	236.3	241.1	257.2	308.7
"(***)	F	5-98-2	10	242.6	308.7	-----	-----
"	L	5-97-2	2	239.9	260.7	293.0	-----
"(***)	L	5-97-1	4	241.1	254.8	310.6	-----
"(***)	M	5-99-1	10	240.3	268.6	296.4	-----
"(***)	C	5-98-1	2	233.1	238.3	250.1	307.2
"(***)	C	5-96-3	4	237.1	250.9	296.8	-----
"	C	5-100-2	10	240.3	273.1	-----	-----

(+). T₂ in this case is the crystal transformation. It was preceded by a small exotherm.

(**). In these cases a small endotherm was noted at about 155-160 degrees.

(***). An endotherm was observed at 142-144 degrees.

Table I (cont.)

(1)	(2)	(3)	(4)	T ₁	T ₂	T ₃	T ₄
Ba(ClO ₄) ₂	F	6-4-1	2	240.3	333.5	-----	-----
"	F	6-2-2	4	239.1	348.4	380.5	-----
"	F	6-8-1	10	244.2	386.9	-----	-----
"	M	6-5-1	2	240.0	238.0	-----	-----
"	M	6-3-2	4	246.2	253.7	-----	-----
"	M	6-8-3	10	241.4	383.1	-----	-----
"	C	6-6-1	2	237.2	343.4	-----	-----
"	C	6-6-2	4	243.3	363.1	-----	-----
"	C	6-10-2	10	241.8	380.6	-----	-----
Mg(ClO ₄) ₂	F	6-7-1	2	237.1	304.8	338.1	-----
"	F	6-8-2	4	237.9	311.0	338.5	-----
"(')	F	6-13-1	10	239.5	337.7	368.0	-----
"	M	6-9-1	2	243.4	383.9	-----	-----
"	M	6-11-1	4	238.3	318.3	337.0	-----
"	M	6-7-2	10	238.7	346.1	363.2	-----
"	C	6-10-1	2	237.5	304.5	357.9	-----
"	C	6-11-2	4	240.3	311.8	333.5	-----
"(')	C	6-12-3	10	239.1	335.4	356.7	-----
NaClO ₄	F	6-12-1	2	240.0	342.3	-----	-----
"(')	F	6-13-2	4	242.6	380.5	-----	-----
"	F	6-14-2	10	239.5	425.5	-----	-----
"('')	M	6-12-2	2	241.4	382.0	-----	-----
"('')	M	6-14-1	4	241.4	398.1	-----	-----
"	M	6-14-2	10	237.5	409.4	-----	-----
"('')	C	6-13-3	2	238.3	363.5	-----	-----
"('')	C	6-14-4	4	237.1	393.3	-----	-----
"('')	C	6-15-1	10	239.5	393.6	-----	-----

('). In these two runs a small endotherm of uncertain cause was noted at 177-179 degrees.

(''). In these runs an endotherm was observed in the region of 213-216 degrees.

Table I (cont.)

(1)	(2)	(3)	(4)	T ₁	T ₂	T ₃	T ₄
KClO ₄	F	5-89-1	2	237.9	351.8	-----	-----
"	F	5-88-1	4	244.6	322.5	372.1	-----
"(")	F	5-90-3	10	243.2	332.8	-----	-----
"	M	5-90-1	2	241.1	362.0	-----	-----
"	M	5-88-2	4	244.6	386.9	-----	-----
"(""")	M	5-90-2	10	243.0	401.1	-----	-----
"	C	5-89-2	2	241.8	361.6	426.6	-----
"	C	5-91-1	4	239.9	385.0	-----	-----
"	C	5-89-3	10	245.4	405.6	-----	-----
Pb(ClO ₄) ₂	F	5-86-1	2	238.3	301.0	326.3	-----
"(")	F	5-87-1	4	242.6	339.6	-----	-----
"(""")	F	5-87-3	10	241.1	343.0	-----	-----
"	M	5-85-1	2	240.3	303.7	318.7	326.0
"	M	5-84-2	4	241.1	345.3	-----	-----
"	M	5-86-2	10	244.2	352.2	-----	-----
"	C	5-83-3	2	239.5	315.6	328.6	-----
"	C	5-84-1	4	241.4	306.8	337.4	-----
"	C	5-87-2	10	243.0	344.2	-----	-----

("). An endotherm was noted in these two cases at 100-103 degrees and most likely was due to water in the sample.

(""). A small exotherm of unknown cause was noted at 84.4°.

(""""). A broad endotherm of small magnitude was noted at about 182 degrees. This is most likely due to water trapped in the crystal lattice.

Table II

Peak temperatures from DTA runs on doped AP samples. (99/1 mole ratio of AP to added metal perchlorate)

(1)	(2)	(3)	(4)	T ₁	T ₂	T ₃	T ₄
NaClO ₄	F	6-18-2	2	236.6	328.1	-----	-----
"	F	6-19-1	4	241.1	327.5	306.3	-----
"	F	6-22-2	10	241.1	300.3	-----	-----
"	M	6-21-1	2	240.7	372.1	-----	-----
"	M	6-20-1	4	240.3	410.5	-----	-----
"	M	6-22-3	10	243.8	416.9	-----	-----
"	C	6-21-3	2	238.3	385.4	-----	-----
"	C	6-22-1	4	237.9	383.5	-----	-----
"	C	6-21-2	10	242.6	401.1	-----	-----
AgClO ₄	F	6-23-1	2	238.3	343.0	-----	-----
"	F	6-25-1	4	241.1	358.2	-----	-----
"	F	6-26-2	10	245.0	342.7	-----	-----
"	M	6-24-1	2	239.5	345.3	-----	-----
"	M	6-25-2	4	241.1	353.2	-----	-----
"	M	6-27-2	10	241.8	357.1	-----	-----
"	C	6-24-2	2	241.1	342.7	-----	-----
"	C	6-23-2	4	239.1	367.3	-----	-----
"	C	6-24-3	10	242.2	400.4	-----	-----
Cu(ClO ₄) ₂	F	6-26-1	2	237.1	245.4	322.2	-----
"	F	6-29-1	4	238.3	250.1	336.2	-----
"	F	6-32-2	10	243.8	305.6	-----	-----
"	M	6-27-1	2	236.3	244.6	324.8	-----
"	M	6-32-3	4	325.9	249.7	331.6	-----
"	M	6-34.1	10	241.1	291.4	359.0	-----
"	C	6-28-1	2	234.3	242.6	322.9	-----
"	C	6-33-1	4	239.1	254.0	338.9	-----
"	C	6-33-2	10	243.4	270.0	356.3	-----

Table II (cont.)

(1)	(2)	(3)	(4)	T ₁	T ₂	T ₃	T ₄
Zn(ClO ₄) ₂	F	6-31-1	2	237.5	251.3	-----	-----
"	F	6-29-2	4	237.1	263.8	-----	-----
"	F	6-34-2	10	237.9	279.4	294.5	-----
"	M	6-31-2	2	233.9	248.2	-----	-----
"	M	6-30-1	4	237.1	270.8	-----	-----
"	M	6-34-3	10	243.0	289.5	-----	-----
"	C	6-32-1	2	237.1	248.9	-----	-----
"	C	6-30-2	4	241.1	270.8	-----	-----
"	C	6-39-2	10	240.7	284.0	-----	-----
Pb(ClO ₄) ₂	F	6-35-1	2	238.3	345.7	-----	-----
"	F	6-35-2	4	237.9	359.7	-----	-----
"	F	6-41-2	10	243.8	272.4	-----	-----
"	M	6-36-1	2	239.5	342.7	-----	-----
"	M	6-40-1	4	238.3	364.1	-----	-----
"	M	6-40-2	10	241.1	372.9	-----	-----
"	C	6-39-3	2	241.4	350.3	-----	-----
"	C	6-40-3	4	243.0	370.1	-----	-----
"	C	6-41-1	10	268.2(?)	370.8	-----	-----